Nanoscale Order in Amorphous Solids: Structure, Transformations and Electronic Properties

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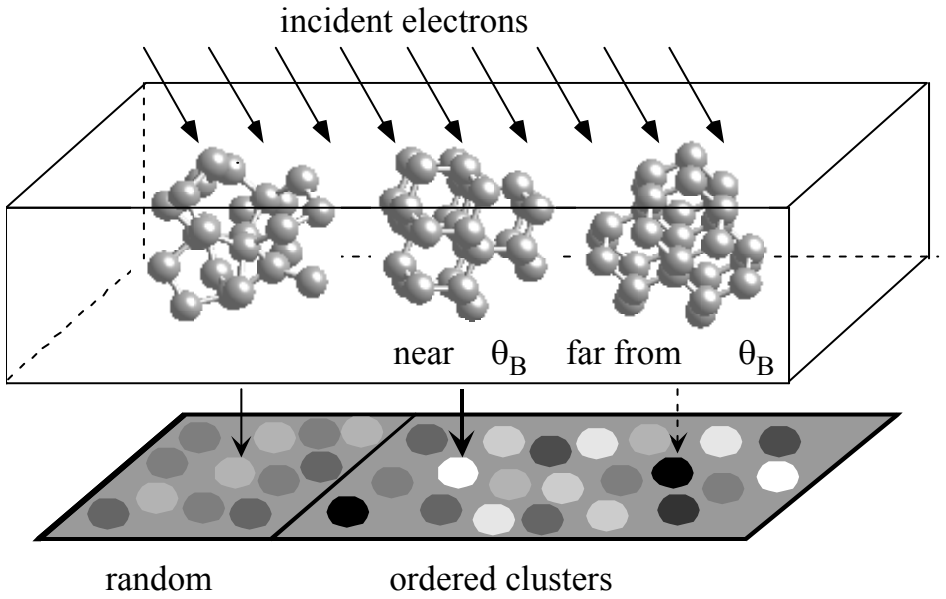
Fluctuation Electron Microscopy in the TEM reveals the presence of nanometer-sized ordered regions in amorphous solids via statistical analysis of the image variance **V** vs. scattering vector *k* at mesoscopic resolution.



Fluctuation electron microscopy (FEM), carried out in the TEM under conditions of mesoscopic (1-2 nm) image resolution, provides statistical information about the presence of topologically ordered regions in amorphous solids. Theory by Gibson & Treacy shows that the data are directly related to 3- and 4-body correlation functions between atomic positions, convoluted over the microscope response function. The 4-body function is sufficient to detect and define the presence of medium range structural order. By contrast, diffraction from an amorphous solid is primarily sensitive to the 2-body correlation function.

The graphic shows, schematically, how FEM works: a sample which is truly amorphous (left) always produces little variance in image contrast; a sample with ordered domains (right) yields a high image contrast at scattering vectors which correspond to Bragg reflection conditions. The sensitivity of the technique occurs because the TEM resolution is intentionally degraded to the mesoscale -- meaning similar to the dimension of the ordered regions -- rather than atomic.

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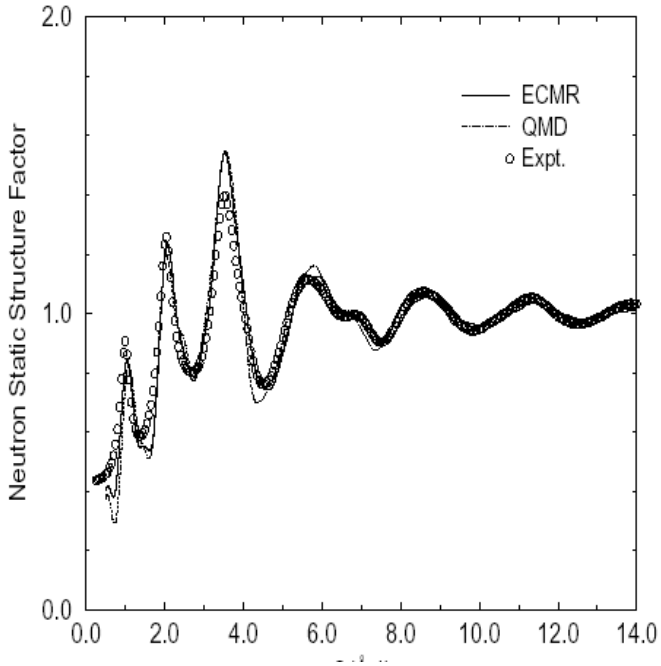
Experimentally Constrained Molecular Relaxation (ECMR): We have developed a new simulation technique to generate model amorphous structures that combines ab initio molecular dynamics with any form of experimental information. Here, we have used ECMR to create a model of glassy $GeSe_2$ that is consistent with the neutron static structure factor and a first principles force field. For the first time the celebrated "first sharp diffraction peak" in S(q) is in good agreement with experiment, suggesting that the model captures the intermediate range order associated with this feature. The electronic density of states (not shown) is also in satisfactory agreement with experiment.



The new method -- ECMR -- is our realization of a "reverse Monte-Carlo" algorithm. An initial model amorphous structure, that may be a random network or a random array of atoms, is modified in a stepwise fashion such that it ultimately fits all the input experimental data and also minimizes the energy of the system via the energy functions associated primarily with short range order. Here, the latter are calculated using ab-initio methods rather than using an empirical potential, such that complex defect structures (highly strained bonds, antisite defects,…) are allowed realistically. Note that many previous attempts to implement reverse Monte-Carlo algorithms were not properly constrained by the short range order, and yielded physically unrealistic (useless) model structures.

Significance: The ECMR method has very general applicability. We have already used it to yield new insights into the medium range order in a-Si and a-GeSe2, and the method can be used to study amorphous metals. We expect it play a major role in our continuing work.

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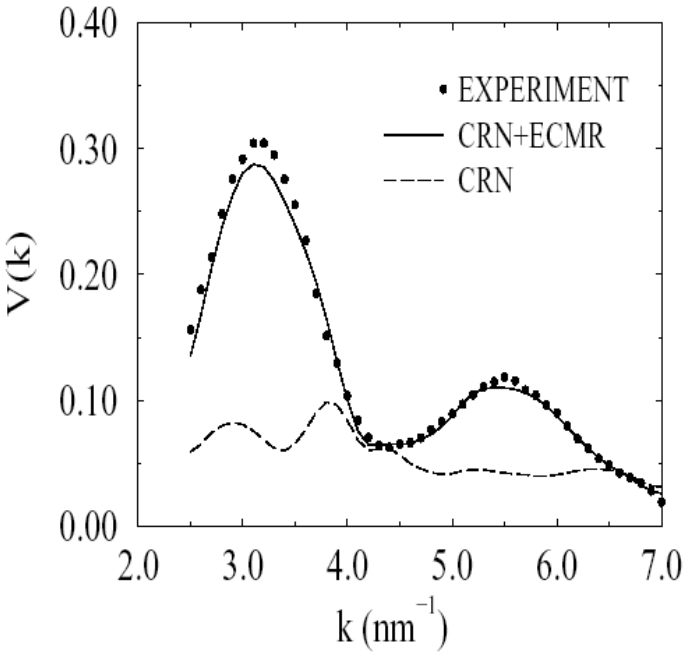
Experimentally Constrained Molecular Relaxation (ECMR): We have developed a new simulation technique to generate model amorphous structures that combines ab initio molecular dynamics with any form of experimental information. Here, we have used ECMR to construct new classes of models of a-Si that agree simultaneously with (1) the pair-correlation function of a-Si, (2) the FEM signal V(k), and (3) first principles interatomic interactions. The model matches the V(k) data but, unlike previous model structures, includes no regions of crystalline order: rather, it exhibits small density fluctuations on the nanometer length scale. The dashed line indicates the V(k) from a CRN (covalent random network) model without MRO.



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CRN means "covalent random network" which is constructed in the computer using the well-tested Wooten, Weiner, Weaire algorithm. A CRN has short range order in agreement with experiment, meaning similar to that in a diamond cubic crystal (nearest-neighbor bond length deviation ~ Gaussian with 1% FWHM, mutual angle between two nearest neighbors centered on 109.5 degrees, deviation ~ Gaussian with 10 deg FWHM). But there is NO topological crystallinity, i.e. no medium range order, in a CRN. The CRN serves as the model for a perfectly amorphous material within the constraints of tetraheral coordination. Using a CRN model, we calculate the fluctuation microscopy variance signature V(k) to serve as a reference to compare with the experimentally measured signal.

Significance: The ECMR method has very general applicability. We have already used it to yield new insights into the medium range order in a-Si and a-GeSe2, and the method can be used to study amorphous metals. We expect it play a major role in our continuing work.

Interest: Above, the ECMR method has yielded a new insight into the MRO in a-Si -- that a class of structures may exist in which the fluctuation microscopy signature V(k) arises from subtle density modulations rather than from small, topologically crystalline regions. Obviously we need to determine what class of structure is correct for a given physical sample. This we plan to do by acquiring FEM data using a scanning-mode TEM (STEM): in this approach, which has been implemented at UIUC, a nanodiffraction pattern is taken from each nm-sized position on the sample; the presence of topologically crystalline regions can be extracted from the variance of each nanodiffraction pattern. The full details of the latter method will appear in our third year report (2005).

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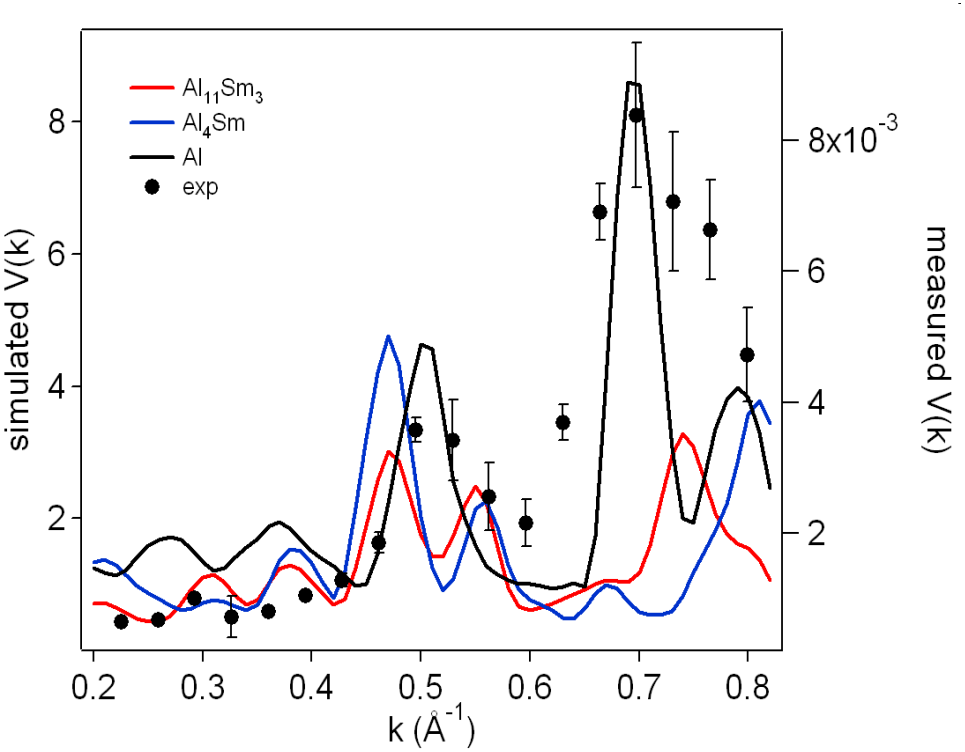
Binary alloys: We developed methods to simulate the fluctuation microscopy signature of nanoscale order in binary alloys. Here, $Al_{92}Sm_8$ metallic glass displays experimental peaks in V(k). Calculations (solid lines) are consistent with the presence of pure Al nanocrystals, but not with the presence of Al-Sm intermetallic compounds or clusters (not shown). The nanocrystals are believed to modify the mechanical properties but had not been previously detected or identified.



For this work we have devised an approximate method to predict the peak positions in the FEM variance signature V(k). A "motif" of each possible crystal structure, essentially equal to a unit cell of the crystal structure, is used to generate scattering statistics. Here, a comparison of the results for Al, $Al_{11}Sm_3$, Al_4Sb_1 shows that only the first qualitatively matches the FEM data. This weights against the possibility that intermetallic precipitates are formed in the metallic glass.

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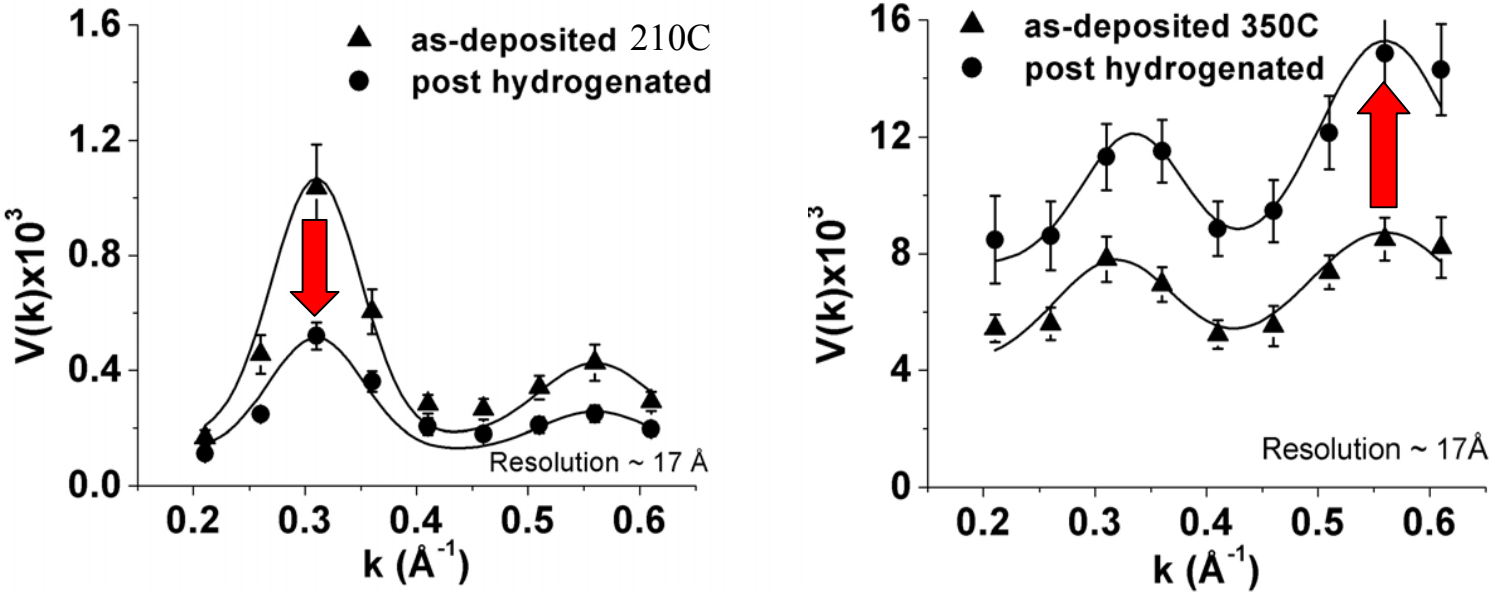

Stability of order: It has often been assumed that regions of medium range order will always increase in size upon network modification. Here, we have prepared a-Si samples with variable amounts of MRO; when the regions are small (left), they shrink upon H exposure, whereas larger regions (right) expand. This indicates a critical size for the stability of regions of MRO, analogous to (though different in detail from) the critical size for a stable nucleus in capillarity theory.

Significance: The result provides clear evidence for the size dependence of the stability of the regions of medium range order. Also, it is not consistent with the V(k) signature being only the result of density fluctuations -- here there must be topologically ordered regions

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Education and outreach: Paul Voyles co-organized a symposium entitled 'Order in the Disorder' as part of the annual Microscopy & Microanalysis Conference (Savannah, August 2004). This meeting, which continued the themes of our previous workshop (UIUC, June 2003), was attended by specialists in amorphous glass, metal, and semiconductor materials, as well as experts in TEM and network topology.

Human resource development: Five graduate students and three post-doctoral scientists have worked primarily on this project. One international student (from France) performed a six month project for his M.S. thesis.